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DETERMINATION OF FREE CARBON IN RUBBER
GOODS

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I. INTRODUCTION

The main object, perhaps, in the determination of free carbon in rubber goods is not the information gained directly, but the opportunity thus permitted for the determination of the rubber content by difference. For some time past the most widely used method for the determination of rubber has been to calculate it as the difference between 100 per cent and the total of the percentages of ash, total sulphur, and the various extracts. Recently refinements on this general method for the determination of rubber have been proposed and quite generally accepted, and it is to-day the standard of analysis. Obviously, this method is subject to wide error when free carbon is present and no correction is made for it.

II. DISCUSSION OF PROPOSED METHOD

A search of the literature on the subject revealed two general methods for such a determination; first, that in which nitric acid is used to decompose and remove the rubber, and the carbon is then determined in the residue; and second, that in which the rubber is dissolved in high-boiling solvents, such as petroleum oils,

nitrobenzene, and aniline, and the carbon is then similarly determined in the residue.

Henry William Jones¹ proposes the use of nitric acid as a means of separating free carbon from vulcanized rubber and describes his process as follows: "A one to two g sample is heated with concentrated nitric acid and then filtered cold on a Gooch crucible, washed with nitric acid to remove the mother liquors and then with water to remove the acid and soluble metallic salts. The insoluble residue is then air dried at ordinary temperatures, weighed, ignited, and weighed again."

W. A. Caspari also² utilizes nitric acid to decompose the rubber, but uses ammonia to remove the nitration products formed.

We found the method of Caspari to give high results, since there is no attempt to remove any organic compounds which may not be dissolved by nitric acid or ammonia. The method of Jones seemed, in general, to be satisfactory. In the report referred to, however, the details are somewhat lacking and the latter part is confusing. In both methods no account is taken of the action of nitric acid on the carbon present.

The outline of our method as we first tried it was, first, primarily to remove organic matter with nitric-acid treatment and then filter on a Gooch crucible, leaving only fillers which were not attacked by nitric acid; and second, to remove by suitable treatment those remaining mineral fillers which might show a loss in weight during ignition of the carbon. The carbon could then be determined by difference in weight before and after ignition.

Our first experiments indicated the following:

1. The carbon itself was liable to attack by nitric acid.
2. The organic matter was not all removed by nitric acid.
3. Lead sulphate seemed to be the chief mineral ingredient which needed to be removed after the nitric-acid treatment.

We treated samples of lampblack and gas black for various periods with concentrated nitric acid. In each case the mixture was heated on the steam bath for a definite length of time and then evaporated to dryness. The residue was always heavier than the original sample, and the increase was from 3 to 5 per cent for the minimum time taken to evaporate off the acid and from 5 to 8 per cent for 15 hours' heating.

We then treated samples of lampblack and gas black for definite lengths of time with concentrated nitric acid, after which we filtered off the solution on a Gooch crucible, washed well with

¹ Paper presented before the Fourth International Rubber Congress.

² India Rubber Laboratory Practice.

nitric acid, then with acetone, and finally with sodium-hydroxide solution. The alkali invariably extracted material the nature of which we did not investigate. The ignition loss of the residue, in proportion to the original amount of carbon taken, varied from 100 to 102 per cent in the case of gas black and from 101 to 105 per cent when lampblack was used.

As yet we have not made any effort to identify the products formed by the action of nitric acid on the variously made forms of amorphous carbon, but are inclined to believe the action is an oxidizing one similar to the formation of graphitic acid by the prolonged heating of a mixture of graphite, potassium chlorate, and nitric acid. Therefore, one would expect to find here complex carboxylic compounds formed by the addition of hydrogen and oxygen to the carbon atoms.

There seem to be at least three classes of compounds formed, namely, the first soluble in nitric acid, the second insoluble in nitric acid but soluble in alkali, and the third insoluble in both. Our experience indicated that the last named was the major product of the reaction.

Our first trials at completely removing the nitrated rubber with nitric acid showed that this was impossible. After filtration from the nitric-acid solution, washing with acetone would invariably give an extract, having in some cases the characteristic yellow of the nitrosite of rubber, in others a deep brown extract which persisted for several washings. With samples giving these deep-brown extracts with acetone, a further washing with sodium hydroxide would result in a second brown extract. This showed that the nitric acid did not remove all of the nitrosite of rubber, in addition to some other organic matter which may or may not have been nitrated, but which seemed to be soluble in acetone or sodium-hydroxide solution. It was noted that the brown acetone and sodium-hydroxide extracts were invariably obtained when mineral rubber was known to be present. As all of the samples nitrated had previously been extracted with acetone and chloroform, we were led to conclude that we were encountering that part of mineral rubber which, according to Caspari, becomes insoluble in the usual solvents after vulcanization.

B. D. Porritt³ confirms Caspari's work, showing that during vulcanization some of the bitumen passed into an insoluble form much as rubber does. In the case of vulcanite, he says that

³ Estimation of Bitumen in Rubber Mixings, Proceedings of Fourth International Rubber Congress.

nearly half of the bitumen is rendered insoluble. He presented no information, however, to show whether or not combination with sulphur takes place. He also found that nitric acid had no apparent action on bitumen. He treated a rubber mixing containing bitumen with nitric acid, and tried to determine by extracting with carbon bisulphide the bitumen left in the residue. He obtained extremely low results. From this he concluded that the preliminary treatment with nitric acid had rendered a portion of the bitumen insoluble in the solvents. If this were the case, carbon determined as we have proposed would give high results.

An experiment which we hoped might disclose the effect of mineral rubber on the determination was made as follows: Some mineral rubber was melted and stirred up with sulphur at 200° C. A vigorous reaction took place with considerable evolution of hydrogen sulphide. The brittle solid product obtained was extracted with acetone and chloroform, and gave a very large insoluble residue. This residue was found to be insoluble in all of the common organic solvents and unattacked by strong sodium hydroxide. When treated with hot concentrated nitric acid for a few minutes, the acid became colored a deep brown, but the larger part of the material persisted as a black floating mass. It remained so even after a 24-hour treatment. This residue, however, we found to be readily soluble in either acetone or strong sodium-hydroxide solution. The effect of mineral rubber on the determination would then be as follows: The preliminary extractions with acetone and chloroform would remove the soluble portions; after nitration, acetone and sodium-hydroxide solutions would remove that part which had become insoluble through vulcanization.

We carried out a large number of determinations on compounds treated directly with nitric acid. We compared these results with results obtained on the same samples which had been extracted with acetone and chloroform before nitration. As a result we would recommend that low-grade stocks be extracted, as it will facilitate the filtration of the nitric-acid liquor. It will be found to be of no material advantage to extract high-grade stocks containing rubber as the only organic matter added to the compound.

Assuming that the organic matter has all been removed by the nitric acid, organic solvents, and sodium-hydroxide solution, there remain with the carbon all of the mineral constituents which were not removed by the nitric acid. Among the latter lead sulphate

is very often present, since part of any litharge present is converted into lead sulphate during the nitric-acid treatment. Any mineral matter remaining which is not attacked by carbon during ignition or which itself suffers no ignition loss obviously need not be removed. If lead sulphate, however, is allowed to remain in contact with the carbon during ignition, it becomes at least partially reduced and perhaps volatilized, with a consequent loss in weight. Lead sulphate is therefore removed by washing with concentrated ammonium-acetate solution until the filtrate shows the absence of lead.

There are a large number of other fillers and pigments which will show ignition losses and will consequently give erroneous results. Some of these may be eliminated by suitable washes, as in the case of lead. The errors caused by others, however, can not be eliminated, but often can be largely reduced by washing with concentrated hydrochloric acid as given in the procedure. The following table shows the approximate ignition losses of fillers and pigments which may be present at this point. For use in case these may be removed by some additional treatment, the methods which we have found to be successful are given:

Material	Ignition loss	Method of elimination
	Per cent	
Talc.....	1.3	
Red iron oxide.....	.15	
French ocher.....	7.0	
Chrome green.....	.1	
Calcium sulphate.....	.15	
Crimson antimony.....	3.3	
Golden antimony.....	3.1	
Tripoli.....	.6	
Soapstone.....	1.3	
Mica.....	3.0	
Rotten stone.....	2.6	
Vermilion.....	(^a)	The vermilion is dissolved by washing the pad repeatedly with hot concentrated sodium sulphide solution.
Brown aluminum flake.....	10.5	The ignition losses can be cut to less than 1 per cent by a treatment with sodium hydroxide, the details of which are given below.
Gray aluminum flake.....	12.8	
Infusorial earth.....	5.0	
Domestic china clay.....	12.9	
English china clay.....	11.4	

^a Completely volatile.

When aluminum flake, china clay, or infusorial earth are present, proceed as follows: After the nitric acid has been allowed to act upon the rubber sample for 1 hour on the steam bath, allow it to

settle for 30 minutes. Pour the supernatant acid liquor through the Gooch crucible and wash the residue remaining in the beaker repeatedly with nitric acid by decantation. Digest with 35 cm³ of a 25 per cent solution of sodium hydroxide for 1 hour. Filter through the same Gooch crucible. Wash the excess alkali from the pad with water and proceed in the regular manner, omitting, however, the washings with 15 per cent sodium-hydroxide solution.

In order to remove the last traces of sodium hydroxide previously used as a wash, the pad was washed well with a very dilute solution of hydrochloric acid. This can not well be followed by a wash with water, since the carbon is apt to go into colloidal solution. On attempting to dry the residue at 200° C, it was found that it gradually decreased in weight, probably owing to the very slow oxidation of the carbon at this temperature. Drying for one and one-half hours at 150° C, however, removed all of the hydrochloric acid and gave a constant weight.

III. DETAILS OF METHOD AS FINALLY ADOPTED

As a result of these preliminary considerations and experiments, we devised the following procedure:

Extract a 1-g sample for six hours with acetone and then for three hours with chloroform or carbon bisulphide. Transfer the sample to a 250-cm³ beaker and heat on the steam bath until it no longer smells of chloroform. Add a few cm³ of hot concentrated nitric acid and allow to stand in the cold for about 10 minutes. Add 50 cm³ more of hot concentrated nitric acid, taking care to wash down the sides of the beaker. Heat on the steam bath for about one hour or until all bubbles or foam disappear from the surface. Pour the liquid, while hot, into a Gooch crucible containing a thick pad of ignited asbestos. Filter by slowly applying gentle suction and wash well with hot concentrated nitric acid. Empty the filter flask and wash the filter alternately with acetone and benzol until the filtrate is colorless. Next wash it well with a hot 15 per cent solution of sodium hydroxide. Test for the presence of lead by running some warm ammonium acetate solution, containing an excess of ammonium hydroxide, through the pad into a solution of sodium chromate. If a yellow precipitate forms, the pad must be washed with the ammonium-acetate solution until the washings no longer precipitate the sodium-chromate solution. Next wash the residue a few times with hot concentrated hydrochloric acid and finally with

warm 5 per cent hydrochloric-acid solution. Remove the crucible from the funnel, taking care that the outside is clean, and dry it in an air bath for one and one-half hours at 150° C. Weigh, burn off the carbon at a dull-red heat, and reweigh. The difference in weight represents approximately 105 per cent of the carbon originally present in the form of lampblack or gas black. It is recommended that 0.5-g samples be taken for compounds containing over 10 per cent of free carbon and 1-g samples for compounds containing less than this amount. It is also unnecessary to extract high-grade compounds.

It will be noted that we have taken the factor 105 per cent as a ratio between the ignition loss and the amount of carbon present. This factor is arrived at from the results of a large number of determinations made at the Bureau of Standards. The results of gas-black determinations ran from 101 to 106 per cent and lamp-black determinations ran from 102 to 108 per cent. Results were obtained on different samples containing large amounts of mineral rubber, lead both in the form of oxide and sulphate, reclaimed rubber of various kinds, glue, substitute, sulphides of antimony, talc, and others. In all cases the results came between 101 and 108 per cent of the carbon originally present. So, by using a factor of 105 per cent the maximum divergence would be 4 per cent and the usual divergence very small.

In our analysis of the gas black and lampblack used in our experiments, we determined the volatile loss at 100° C, the acetone-extractable matter and the ash, and assumed the remainder of our samples to be carbon. Our results have been calculated on this basis.

IV. SUMMARY

1. It is necessary to correct the result as obtained by ignition loss to compensate for the error caused by the formation of compounds from the free carbon.

2. The attack of amorphous carbon by nitric acid renders an accurate determination by this method impossible; nevertheless the error caused thereby is sufficiently uniform and small in magnitude to allow of a practical determination.

3. The presence of certain mineral fillers will give rise to error. The error caused thereby, however, is usually small. In case accurate results are desired when these fillers are present, an analysis of the mineral matter should be made and proper corrections applied.

4. Assuming the ignition loss to be 105 per cent of the weight of carbon, we feel that the results by this method justify its use at present as a routine method in the rubber laboratory.

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